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A Study on Brightness Improvement and Deterioration of ZnS:Cu Electroluminescence

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The main purpose of this paper is on studying to improve the brightness properties, to understand the aging properties, and to suggest the protection layer of ZnS:Cu electroluminescent device. To improve the brightness that is totally related electrical, material and optical properties, the new type of device structure that started from the idea of luminescent mechanism [1] was suggested. By changing the device structure (ITO film/ZnS:Cu/$BaTiO_3$/Ag, ITO film/ZnS:Cu+$BaTiO_3$/Ag), more high brightness and improved blue emission properties of ZnS:Cu powder EL could be obtained. Also, one of important things in operation, the deterioration property [2] was investigated to get the aging reasons and the protective method from the moisture and ultraviolet. At room temperature and 70℃ relative humidity 100% condition respectively, the continuous operation properties were experimented and the deterioration mechanism of ZnS:Cu was investigated by the concentration of sulfur vacancy and deep trap. Additionally the protective method from moisture and water was suggested by panylene(poly-para-xylene) polymer coating.

The following materials are required in preparation for powder EL device; the organic binder of the high dielectric, the phosphor powder, the dielectric powder, the transparent electrode film and the silver paste for back electrode [3~5]. Cyanoresin (CR-S, Shin-Etsu Chemical Co. Ltd) was used as a binder and N.N- Dimethylformaid (Junsei Chemical Co. Ltd), the solution of CR-S was mixed in concentration 10~40 weight percent. To dissolve CR-S it agitated until the solution becomes viscous and clear. ZnS:Cu (99.9%, Sylvania) which average grain size is about 20㎛ was used as a phosphor and it was mixed with the binder solution as the ratio of 1:2 (binder/ZnS:Cu) in weight. $BaTiO_3$ (99.9%, Aldrich) was used as a dielectric and it was also mixed with the binder solution as the ratio 1:3 in weight. ITO-film (300Ω/□,Toray 125L) for the transparent electrode and silver paste for the back-electrode were respectively used.

Using the scanning electron microscope (SEM) and photomicrograph, the surface and cross sectional properties were observed to identify the structure of the fabricated devices as figure 1. Especially the comparative change of particles were measured when voltage were applied or not applied.

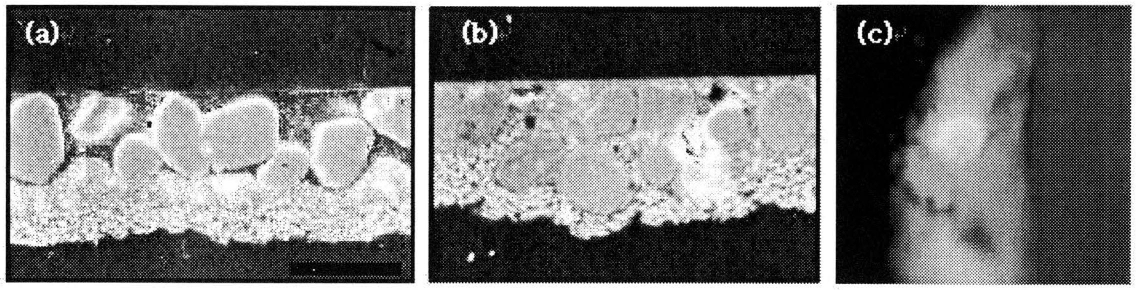

Figure 1. The cross-sectional SEM photographs of ZnS:Cu EL
:(a) ITO film/ZnS:Cu/$BaTiO_3$/Ag, (b) ITO film/ZnS:Cu+$BaTiO_3$/Ag (c) Emission of ZnS:Cu particle

The spectroscopic properties were analyzed by diode array type monochrometer (PSI, Darsa-2000). CIE coordinate system and brightness was measured by luminance meter (Minolta, LS-100). The sine wave power supply which can control AC 0~300 V voltage and 60~20,000 Hz frequency, was used. To understand the optical and structure property with the wave change of applied voltage, the decay scope was measured as figure 2.

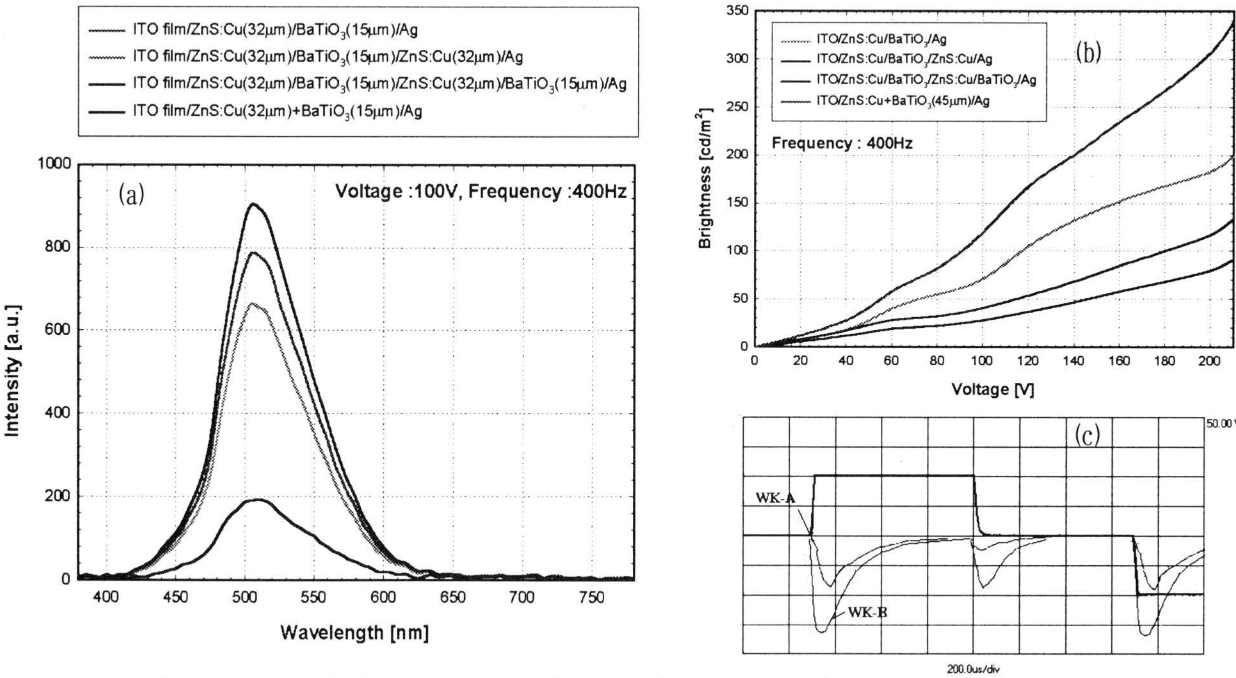

Figure 2. The emission spectrum, brightness and decay scope with different device structure
:(a) Emission spectrum, (b) Brightness variation, (c) Decay scope

The aging properties of conventionally structured ITO-film/ZnS:Cu/$BaTiO_3$/Ag paste were experimented respectively at room temperature and 70□, relative humidity 100%. While AC 100V on 400Hz frequency were applied to the devices, the change of brightness were measured and compared as figure 3. Also, the surface of aged devices was investigated by photomicrograph. The powder EL devices were located on the top of water-bath. The condition of 70℃, relative humidity 100% controlled by heating the water in water-bath.

The proposed deterioration mechanism is accessible to a semi-quantitative analysis. Let the time-average of steady-state emission be L= β /M where M is the concentration of deep traps in the particle volume, and where β represents all other parameters. It must be supposed that the traps denoted by M are deep enough that a captured electron has little chance of escape during one cycle of the applied frequency.

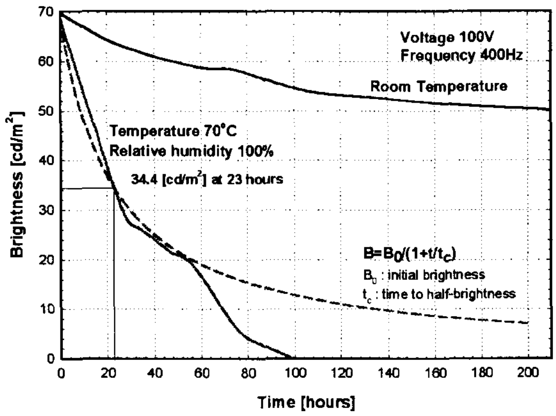

Figure 3. The deterioration curve measured on brightness decay, at room temperature and 70℃ relative humidity 100%

The concentration of sulfur vacancies at or near the surface may be C. When they diffuse into the volume, the decrease at a rate proportional to C, which gives $C = C_0 \exp(-\alpha t)$ where C_0 and α are constants, and t is the time. Simultaneously, the concentration of deep traps in the volume increases with the same rate $dM/dt = -dC/dt = \alpha C_0 \exp(-\alpha t)$, which gives $M = M_0 + C_0[1-\exp(\alpha t)]$.

Hence, the emission intensity at any given time, normalized to the "zero-hour" intensity L_0, is

$$L/L_0 = M_0/M = \{1+(C_0/M_0)[1-\exp(-\alpha t)]\}^{-1}$$

This is a function of the ratio L/L_0 on the variable αt which one parameter, the ratio C_0/M_0.

The function is shown in figure 3 where the curves with the lowest ratios of C_0/M_0, i.e., those representing the best maintenance, do approach rather substantial values of L/L_0 for $\alpha t \to \infty$. In contrast, the curves with high values of C_0/M_0, representing poor maintenance, do not only go down very soon, they also approach finite values of L/L_0 very close to zero.

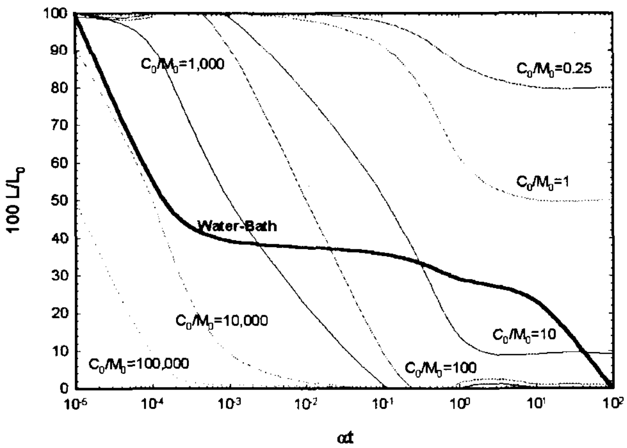

Figure 4. The investigation for the concentration of sulfur vacancy and deep trap

These equations represent ideal cases only. In practice, the situation most certainly is obscured by many complications so that a more detailed calculation seems to have little sense. One complication is the fact that all real phosphors contain particles of many different sizes and, hence, different deterioration rates. If the deterioration curve of such real phosphor containing a wide particle size distribution is analyzed, one finds that the curve becomes somewhat shallower but never steeper than the ideal curves described by Eq.

[3]. The one is also in agreement with experiment. Figure 4 show the deterioration curve measured on a real phosphor (a standard ZnS:Cu,Cl), which, indeed, is shallower than the ideal curves. The other experimental curve in figure 4 is that measured on a single emitting spot inside of one particle. One may safely assume that we are much closer to ideality in this case than in the case of a phosphor containing many particles and, indeed, the experimental curve follows the ideal ones very closely.

The proposed mechanism of a sulfur vacancy migrating from the particle surface into the volume is of course, still a very crude approach to reality. Other atomic or ionic diffusions may occur besides those of sulfur vacancies. It is also possible that the assumption of only the outermost surface of a particle to be of influence is too extreme and that, in reality, surface near layers several atoms deep are involved.

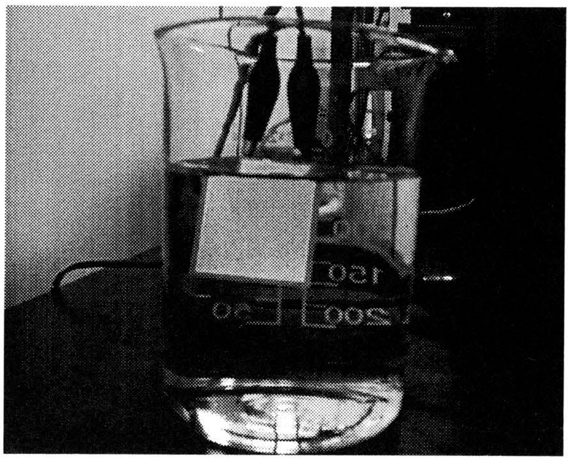

Figure 5. Waterproof operation of powder EL device

Above result of figure 4, the protective method from moisture and water was suggested by panylene(poly-para-xylene) polymer coating. Thus ZnS:Cu powder EL device could operate in water as figure 5.

In conclusion, ITO film/ZnS:Cu+$BaTiO_3$/Ag by the structure change was possible to make more high brightness and improved blue emission properties of ZnS:Cu powder EL. At 100V, 400Hz their brightness was 125 cd/m^2. The deterioration mechanism was approached by sulfur vacancy and deep traps concentration. New type of protective method from moisture and water was suggested by panylene(poly-para-xylene) polymer coating.

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